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Determination of heavy metals concentration in commercially available garlic (*allium sativum*) in Balochistan by atomic absorption spectrometry

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Abstract

'Allium sativum' name of garlic is extracted from the Celtic word 'all' (meaning burning or stinging), and the Latin word 'sativum' (meaning cultivated). In the history, people have used garlic to relieve stomach aches, lower fevers, combat infections, and treat earaches, leprosy, deafness, severe diarrhea, constipation, and parasitic infections. For thousands of years, people have utilized garlic and its derivatives to treat ailments. It is also used at domestic level and in field of pharmaceutic. The current study was done for determination of main seven heavy metals (Mn, Co, Fe, Cd, Cu, Ni and Pb) in garlic by using the atomic absorption spectrophotometer (AAS). From literature review and previous study, it is naked to researchers that heavy metals have highly adverse and negative effect on human beings and their environment. During this study, the determined concentration of all heavy metals in garlic samples, which were collected from Quetta's fruits and vegetables main markets, were compared with accepted standard MPL for heavy metals at international level by WHO/FAO, ATSDR (1994), Codex General Standards for Contamination & Toxin in Foods (1996) and European Union (2006) and it was observed that there were no significant metal who crossed the MPL except Cobalt (in Sample # 2) slightly which may be due to soil, water, fertilizers and concerned environment where the sample was cultivated. Finally, the result was concluded that all heavy metals in garlic samples were within safe range for mankind use in all aspects.

Keywords: AAS, garlic, heavy metals, Quetta.

INTRODUCTION

Metals may be found into a variety of forms and wires and are excellent heat and electrical conductors. Heavy metals are a class of metals that have large densities (>5g/cm³) and toxins. Both plants and animals need them in sufficient amount for survival. High levels of heavy metal consumption might cause serious illnesses or anomalies.^[1] Analysis of harmful atoms in various consumable products, such as garlic, fruits, herbal products, livestock, drinks, and other types of foods, is the primary work

for researchers and nutritionists. It's important to keep an eye on the amount of harmful elements in vegetables and fruits if you want to eat a healthy diet. For proper metabolic activities and bodily growth, minerals are required, and they are also crucial for the formation of vitamins, minerals, and fibers.^[2] Metals are present on earth's surface naturally. Anthropogenic activities such as the use of chemical pesticides, polluting water, drilling, fertilisers, and industrial pollutants can cause food to become contaminated.^[3] (Khan et al., 2019) detailed the defilement of vegetables by toxic elements.^[4]

"Allium sativum" name of garlic is extracted from the Celtic word 'all' (meaning burning or stinging), and the Latin word 'sativum' (meaning cultivated).^{[5][6]} From the Anglo Saxon 'spear plant or gar-leac', the English word 'garlic' is derived, referring to its flowering stalk.

In the history, people have used garlic to relieve stomach aches, lower fevers, combat infections, and treat earaches, leprosy, deafness, severe diarrhea, constipation, and parasitic infections. For thousands of years, people have utilized garlic and its derivatives to treat ailments.^[7]

More than 70% of Pakistan's population relies on agriculture, making it a large agricultural nation. Agriculture is the foundation of Pakistan's economic development and progress.^[8]

Agricultural view of "Garlic", More than 25 million tonnes of garlic are grown annually on more than 6 million acres worldwide, according to the Food and Agriculture Organization of the United Nations. Garlic is farmed in more than a hundred nations around the world, according to the FAO's average-based assessment. In one of the top twenty global producers of garlic is now Pakistan. In terms of global output, China tops the list, followed by India, Bangladesh, Egypt, South Korea, and Russia.^[9]

When we look over garlic agriculture in our country, Pakistan produces 70,925 tonnes of garlic on 7,882 hectares, with an average output of 8.99 tons/ha. Khyber Pakhtunkhwa (KPK) is the main producer of garlic, with an average output of 32,205 tonnes, followed by Punjab (24,143 tonnes), Balochistan (7,880 tonnes), and Sindh (6,557 tonnes), in that order. Balochistan's portion, with 7,880 tonnes, was little and low when compared to the other provinces of Pakistan. Other areas of Balochistan also produce garlic, but the Sibi division, where the district Ziarat is the primary growing area, contributes 40% of the nation's total production.^[8]

Ecologists are worried about the presence of minerals in the surroundings and their biological influence on human body. Food is the main cause of toxic metals which directly affect the human health. Several studies have been carried out for the purpose of the consumption of suitable levels of toxic metals through diet and their need for human body.^[10] Some heavy metals like Cd, Pb and Hg are main toxins for humans through food consumption while others metals (i.e., Cu, Fe and Zn) are crucial for organs of human in their biological processes.^[11]

Toxic residues have been linked to severe neurological conditions, genetic issues, kidney failure, heart problems, and many brain cancer types.^[12] Heavy metals like cadmium can lead to a number of illnesses, like: heart, kidneys, liver, blood vessels, anemia, digestive tract, brain tumors, and genitalia.^[13] High blood pressure is caused by storing cadmium in body.^[14] Nickel poisoning can result in delayed renal bladder growth, disruption of bodily development, and several types of cancers, including blood, bone, and brain cancer.^[15] Remember that all these poisonous outcome of toxic atoms on

living body, we aimed to determine the concentration of toxic/heavy elements in commercially available 'garlic' in Balochistan.

With culinary and medicinal applications dating back to ancient civilizations including Chinese, Indian, Egyptian, and Greek, garlic (Allium sativum L.) is the second-most important Allium crop.^{[16][17]} Due to its strong flavour, this Allium crop is now widely consumed as a popular condiment and green vegetable.^[18] The antibacterial, antifungal, anticancer, and antiviral effects of garlic are currently being claimed.^[19] It aids in the prevention of a number of illnesses, such as cancer, high blood pressure, high cholesterol, and atherosclerosis.^{[20][21]} The literature states that in addition to studies on the possible medical benefits of garlic, studies on the multi-element assessment of trace metals in garlic samples have been conducted to evaluate heavy metal contamination, evaluate the mineral content, and discriminate the product variety.^{[22][23][24][25][26][27]}

In garlic bulbs, there are thirteen trace metals (Li, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Nb, and Mo) and two hazardous elements (Cd and Pb) are studied.^[28] Heavy metals are carcinogenic for our body, therefore, this study had aimed to determine the heavy metals concentration in garlic by using atomic absorption spectroscopy (AAS) technique and compare the all results with standard accepted MPL for heavy metals by international organizations.^[29]

MATERIALS AND METHODS

Sample collection (Sampling)

The garlic samples were collected from Quetta's fruits and vegetables main markets (Kassi road and Hazar-gan-gi) and brought to the research laboratory of the Department of Chemistry, University of Balochistan, Quetta, under well sterilized conditions at room temperature. Labeling and areas of samples are shown in table 1.

| Sr# | Label of Sample | Area of Sample |
|-----|-----------------|------------------|
| 1 | Sample 1 | Zhob |
| 2 | Sample 2 | Killa-Saif-Ullah |
| 3 | Sample 3 | Loralai |
| 4 | Sample 4 | Killa-Abdullah |
| 5 | Sample 5 | Mussa-Khail |
| 6 | Sample 6 | Harnai |
| 7 | Sample 7 | Panjgoor |
| 8 | Sample 8 | Nasirabad |

Table 1. Garlic samples from various districts of Balochistan

Washing, Drying and Grinding

The collected samples were washed with distilled water to remove dust particles. Moreover, peel of garlic clove were removed by the help of stainless steel knife and cuts it into small pieces. And after it, the samples ware dried in oven at temperature of 100°C until constant weight was acquired. The dried samples were grinded separately one by one by using a ceramic mortar and pestle. Such fine grind powder of samples were stored within pre-labeled clean plastic vials for further use. Figure 1 shows parts of garlic, oven, sample within oven and semi powder form of garlic sample in ceramic mortar.



Figure 1. With the help of these pictures we can imagine the visual process of sample preparation.

Digestion

Two grams (2g) of the pre-prepare dried sample was added to 10 ml of concentrated nitric acid within a 50 ml Pyrex beaker and heated upto 80°C on a rotating electric hotplate for a specific time unless the brown fumes were evolved. Thereafter, 10 ml of concentrated perchloric acid was poured into same beaker, and kept it on rotating electric hotplate at same temperature till transparent solution was obtained; then the heating process of beaker was stopped and cooled the beaker at room temperature. The same solution of sample within beaker was diluted upto 50ml mark by using 2% HNO₃ solution. With the help of Whatman filter paper 'number 42', the sample was filtered and kept in neat plastic vial for further analysis. Same process of digestion was fallowed for each and every collected powder sample.

Instrumentation and Metals Analysis

The analyte of interest in samples were analyzed by using Thermo Scientific Electron Corporation-SOLAAR S Series AA Spectrometer System, S. No, GE711544, China (Shown in figure 2). For the investigation analytes, double beam and deuterium background hollow cathode lamps of Fe, Pb, Cd, Co, Cu, Ni, and Mn were utilized at particular wavelengths.



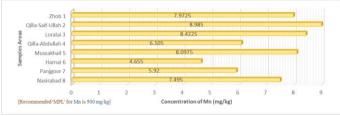
Figure 2 Atomic Absorption Spectrometer.

RESULTS AND DISCUSSION

In this research, verious concentration of metals (Mn, Co, Fe, Cd, Cu, Ni and Pb) within samples, which were collected from Quetta's fruits and vegetables main markets, were determined by AAS technique depending upon samples' areas and there results were compared with standard accepted MPL for heavy metals by international organizations.^[29] Such report is briefly given below:

Manganese (Mn)

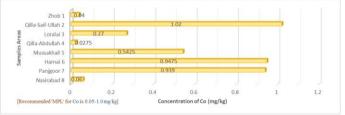
It is an essential trace metal that supports the metabolism of proteins, carbs, and cholesterol. It is also function as an antioxidant. Mn is uses at a rate of 2 to 5 milligrams per day and is stored in the bones, skin, liver, and kidneys.^[34] After examination through AAS, the concentration of Mn in all garlic samples was within safe range by comparing with Mn standard MPL value (500 ppm) and it is briefly elaborated by the help of graph '1':



Graph.1 Concentration of Manganese

Cobalt (Co)

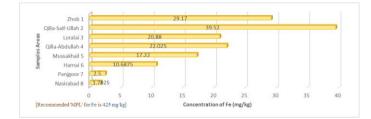
It is naturally occurring metal. Cobalt is a crucial component of vitamin B12, and functions similarly to manganese and zinc. Less amount of Cobalt within human body results anemia. Human toxicity results from consuming more than 30 mg/day of cobalt, which can cause congestive heart failure by changing the structure of the heart muscle and cause issues with the skin and digestive system.^[35] In present study, from graph '2', the result have been concluded that the sample number 2 (Qilla-Saif-Ullah) has slightly crossed the MPL (0.05-1.0 ppm) by '1.02ppm' and the concentration of cobalt within all the remaining samples were founded in safe limit according to standard MPL:



Graph.2 Concentration of Cobalt

Iron (Fe)

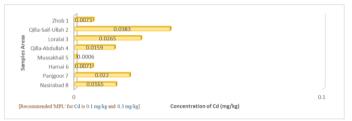
Iron is a very important element for human body which is a main part of enzymes, protein and hemoglobin structures. The gases shifting in human body and metabolism are also carried out in presence of iron.^[31] After the examination of all samples by AAS, the concentration of iron within all garlic samples, which were collected from Quetta's main fruit and vegetable markets, were seen in risk-free range with respect to standard MPL (425 ppm) for iron. Graph '3' shows the complete details about concentration of iron metal within garlic samples:



Graph.3 Concentration of Iron

Cadmium (Cd)

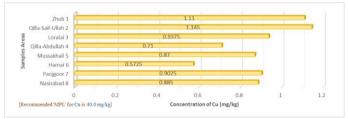
A higher intake of cadmium by humans will have negative impacts on their bodies. It can lead to cancer and harm the skeleton and kidneys.^[33] The concentration of cadmium metal has been detected within safe range for all garlic samples according to standard MPL (0.1ppm and 0.3ppm) which can be seen in graph '4':



Graph.4 Concentration of Cadmium

Copper (Cu)

In industries, the Copper uses for various applications. Paper and pesticides industries are the basic sources of copper. The consumption of copper in greater amount produces negative effect on human health like vomiting, skin irritation, stomach nausea, blood pressure and etc.^[31] After complete examination, concentration of copper metal in all garlic samples were founded less then standard MPL (40.0ppm) for copper metal which were shown in graph '5' brifly:



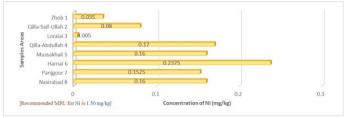
Graph.5 Concentration of Copper

Nickel (Ni)

The Nickel comes in category of trace heavy metals which founds within several enzymes in humans, plants and micro-organisms. In the absorption process of Iron from intestines it plays a role as co-factor and immune system becomes completed with

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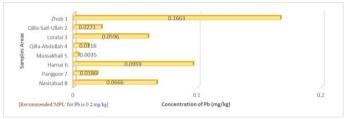
presence of Nickel metal. The more consumption of Nickel by humans creates adverse effect on its health due to increasing heart size and decreasing main body and liver weight.^[30] After thorough investigation of all collected garlic samples, the concentration of Nickel was seen below than standard MPL (1.50ppm) for Nickel metal and the graph '6' explains the complete investigation:



Graph.6 Concentration of Nickel

Lead (Pb)

Being a non-essential heavy metal, the Lead is highly toxic to earth's biosphere and the living things within it; the minute amount use of Lead metal causes severe environment and health issues in humans like damage CNS (central nervous system), bones problem, increases chance of birth abnormalities and miscarriages in women, increase infertility in men.^[32] The environment is contaminated by Lead through exhausts of automobiles and use of pesticides mainly.^[33] After the careful study of garlic samples, the concentration Lead metal was detected within safe region by ASS technique according to accepted standard MPL (0.2ppm) for Lead metal. The Graph '7' distinguished the concentration of lead metal in all garlic samples:



Graph.7 Concentration of Lead

CONCLUSIONS

In the history, people have used garlic to relieve stomach aches, lower fevers, combat infections, and treat earaches, leprosy, deafness, severe diarrhea, constipation, and parasitic infections. For thousands of years, people have utilized garlic and its derivatives to treat ailments. It is also used at domestic level and in field of pharmaceutic. During this study, at last, the determined concentration of heavy metals of collected garlic samples were compared with accepted standard MPL for heavy metals at international level and it was observed that there were no significant metal which crossed the MPL except Cobalt (in Sample # 2) slightly which may be due to soil, water and fertilizers where the sample was cultivated. Finally, the result was

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concluded that all heavy metals in garlic samples were within safe range for mankind use in all aspects.

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